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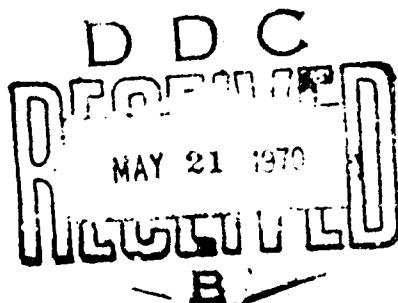
CHEMISTRY, KINETICS AND THERMODYNAMICS

BY

JAMES H. BIGELOW

TECHNICAL REPORT NO. 70-2

MARCH 1970



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Department of Operations Research
Stanford University
Stanford, California

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CHEMISTRY, KINETICS AND THERMODYNAMICS

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I. INTRODUCTION

In this paper, the first of a series of three**, we will discuss the equivalence of three ways of viewing the classical chemical equilibrium problem. From the point of view of classical chemistry, this problem can be stated as follows: Given the set of reactions that may occur among all the species of a chemical system, their equilibrium constants, and the initial composition of the system (i.e. the amounts of each species present in the system initially), find the equilibrium composition of the system.

From the point of view of kinetics, the problem is to determine the evolution of the various parameters describing the system from their initial values. When the parameters cease to change, the system must be in equilibrium.

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**The other two papers are, in order, "Degeneracy in Ideal Chemical Equilibrium Problems," and "Computing Equilibrium Compositions of Ideal Chemical Systems."

Given the same system, thermodynamics seeks that composition at which the usable (or free) energy remaining in the system is at a minimum. It can be shown that the system will then be at equilibrium.

Much of the materiel contained herein is old. It is presented here in a consistent notation, and in a way intended to emphasize the common aspects of the three points of view.

II. CLASSICAL CHEMISTRY

Classically, the composition of a single- or multi-phase chemical system in equilibrium has been computationally determined by solving certain systems of simultaneous equations. These equations included linear equations (mass balance laws) as well as nonlinear equations (mass action laws). It is possible, however, to formulate the problem as one of minimizing a particular nonlinear function (the free energy) subject to linear constraints. This was first done by J. Willard Gibbs [1], in his famous paper "On the Equilibrium of Heterogeneous Substances." It was later shown in a different way, and the equivalence proved with greater mathematical rigor by Shapiro and Shapley [2]. This section restates the first part of Shapiro and Shapley.

1. The Chemical System

We will consider chemical systems composed of a finite number (not excluding one) of homogeneous phases. A homogeneous phase is a mixture of chemical species which is homogeneous in chemical composition, pressure, and temperature. The question of under what circumstances a phase should be regarded as homogeneous can only be answered as part of the process by which we formulate a model of an actual chemical system.

For example, a chemical system consisting of a vapor over a liquid solution might be regarded as having two phases, a gas phase and a liquid phase. A chemical system

consisting of two solutions separated by a semipermeable membrane might be regarded as having two liquid phases.

All this model requires of a phase is homogeneity. A phase need not, for example, occupy contiguous portions of space. Thus in [3], the interiors of all the red blood cells of the body are usefully regarded as forming a single phase.

The entities in a phase are called species, by which we mean molecular species. Examples of species are H_2O , $NaCl$, Na^+ . When a species is defined, its molecular or ionic structure is implied, as well as the number of atoms of each element composing a molecule of the species. Thus the molecular formulas of two distinct species might be identical. (An example of this would be right-handed and left-handed amino acids.) Also, we will find it mathematically convenient to regard a species which can occur in two different phases as two different species. Thus if H_2O can occur in both a liquid phase and a gaseous phase, we would refer to two different species H_2O , perhaps calling them H_2O liquid, and H_2O -vapor. When a molecule moves from one phase to another (by evaporation, condensation, migration across a semipermeable membrane, or black magic) we will regard a type of chemical reaction as having occurred.

By saying that a species can occur in a given phase, we do not mean that at equilibrium any positive amount of that species will be found in the phase. We only mean that we have made provision for the possibility. The

question of which species should be provided for in what phases can only be answered by judgment and experience, and by some knowledge of the system under study.

It should be pointed out that if a phase is a chemical solution, then the solvent itself is one of the species occurring in that phase.

We number the species in the chemical system 1, 2, ..., n. Let x_j be the number of moles of species j in the system. (By definition, a mole is Avogadro's number of molecules, approximately 6×10^{23} .) We denote the phase containing species j by $\langle j \rangle$, and we may indicate that species j and k are in the same phase by writing:

$$j \in \langle k \rangle, \quad \text{or} \quad k \in \langle j \rangle \quad \text{or} \quad \langle j \rangle = \langle k \rangle.$$

Each phase has associated with it a sum,

$$(II.1.1) \quad \bar{x}_{\langle k \rangle} = \sum_{j \in \langle k \rangle} x_j.$$

Each species has associated with it a mole fraction,

$$(II.1.2) \quad \hat{x}_j = x_j / \bar{x}_{\langle j \rangle}.$$

It is easy to see that \hat{x}_j is the concentration (on the mole fraction scale) of species j when the system has composition $x = (x_1, x_2, \dots, x_n)$.

2. The Mass Balance Laws

Following [4], we will express the mass balance laws as linear conditions on x . Let $B_1, \dots, B_1, \dots, B_m$ be a set of fundamental building blocks, such that each species j is a unique combination of these building blocks.

For example, $B_1, \dots, B_1, \dots, B_m$ might be taken to be the atomic elements. However, it is often better to choose more complex structures as building blocks. (See [4] and [5].) Let each molecule of species j contain a_{ij} units of B_i . Thus, the vector $(a_{1j}, a_{2j}, \dots, a_{mj})$ is essentially the molecular formula for species j . Note there is nothing to prevent two different species from having identical molecular formulas. Let b_i be the total number of units of B_i in the system. We then have the conditions:

$$(II.2.1) \quad \sum_{j=1}^n a_{ij} x_j = b_i.$$

The description of those aspects of the system concerned with such questions as which species are permeable to interphase boundaries can be implemented by an appropriate extension of the set of fundamental building blocks. This process has been described elsewhere [4]. In addition, it may be desirable to impose a condition of electrical neutrality on one or more phases. This too may be expressed in the form of (II.2.1) ([2] p. 357). Other

constraints, such as those on the volume of a particular phase, can be similarly handled.

Finally, from the definition of x_j , it is clear that we must have

$$(II.2.2) \quad x_j \geq 0 .$$

3. Reaction Vectors and the Stoichiometric Conditions

In equilibrium chemistry, a reaction is described by writing two formal sums separated by a double arrow. If we denote by N_j the name or chemical symbol of species j , then a reaction would be described by the "equation"

$$(II.3.1) \quad \sum r_j N_j \rightleftharpoons \sum p_j N_j .$$

Each of the terms in (II.3.1) consists formally of a positive real number, r_j or p_j , called a stoichiometric coefficient, multiplied by the symbol for some chemical species of the system. The species occurring in the left-hand formal sum with a positive coefficient r_j are called reactants; the species occurring in the right-hand formal sum with a positive coefficient p_j are called products. The two formal sums separated by a double arrow form the stoichiometric equation of the reaction. Note that mathematically speaking, the stoichiometric equation is not an equation at all, unless the N_j are interpreted as vectors.

We can measure the extent to which the reaction (II.3.1) takes place by an extent of reaction parameter ξ . "Equation" (II.3.1) is interpreted to mean that if the extent of reaction ξ changes to $\xi + d\xi$, then an amount $r_1 d\xi$ of species N_1 , $r_2 d\xi$ of species N_2 , ..., and $r_n d\xi$ of species N_n have reacted to form an amount $p_1 d\xi$ of species N_1 , $p_2 d\xi$ of species N_2 , ..., and $p_n d\xi$ of species N_n .

Given any such stoichiometric equation, we shall define a vector θ , with components θ_j , ($1 \leq j \leq n$) by viewing the expression (II.3.1) as though it were a mathematical vector equation, and treating the double arrow (\rightleftharpoons) as though it were an equals sign ($=$). Bring all the terms to the left (changing the signs in the process), and collect the coefficients of each N_j . Then if we let:

$$\theta_j = r_j - p_j$$

we will have the "equation":

$$(II.3.2) \quad \sum_{j=1}^n \theta_j N_j \rightleftharpoons 0.$$

We call any vector θ so obtainable from a reaction a reaction vector. Observe that different reactions may have the same reaction vector.

As a condition that θ be a reaction vector, we have that:

$$(II.3.3) \quad \sum_{j=1}^n a_{ij} \theta_j = 0 \quad (1 \leq i \leq m)$$

where the a_{ij} are those of equations (II.2.1). The condition can be made sufficient as well as necessary; in actual practice, the model maker judiciously designs (II.2.1)—that is, determines the a_{ij} —so that (II.3.3) will be a sufficient as well as a necessary condition. (For a simple example, see [2], pp. 358-359.) We shall regard any vector θ that satisfies (II.3.3) as a reaction vector.

While (II.2.1) and (II.3.3) are closely related, they are not identical. Unfortunately, the chemical literature refers to both sets of conditions as mass balance laws. We shall reserve the term "mass balance laws" for (II.2.1) and call (II.3.3) the stoichiometric conditions.

4. The Mass Action Laws

For the time being, we shall confine our attention to systems which exhibit the simplest form of the mass-action laws. Such systems are called "ideal" in [6]. A further discussion of ideality can be found in [7]. We will discuss nonideal systems in a later section.

The mass action laws can be stated as follows: For any reaction having a reaction vector θ , there is an equilibrium constant $k(\theta)$, such that, for any composition vector x representing an equilibrium state of the system, we have

$$(II.4.1) \quad \prod_{j=1}^n x_j^{\theta_j} = k(\theta).$$

Note that $k(\theta)$ does not depend on x . (II.4.1) is a condition that x must satisfy if it is to be an equilibrium composition.

We shall find it useful to perform certain manipulations on (II.4.1). Let us first take the logarithm of each side to get:

$$(II.4.2) \quad \sum_{j=1}^n \theta_j \log x_j = \log k(\theta).$$

Equation (II.4.2) is thus satisfied for all reaction vectors θ_j , that is, for all vectors θ which satisfy the stoichiometric conditions (II.3.3). It should be noted that the form of (II.3.3) implies that if α and ϕ are two

reaction vectors, then $(\alpha\theta + \beta\varphi)$ is also a reaction vector, for any real numbers α and β . By the same token, the form of (II.4.2) shows that for the same θ and φ ,

$$\log k(\alpha\theta + \beta\varphi) = \alpha \log k(\theta) + \beta \log k(\varphi).$$

Thus $\log k(\theta)$ is a linear function of θ , so that there must exist constants c_j such that:

$$(II.4.3) \quad \log k(\theta) = - \sum_{j=1}^n c_j \theta_j.$$

Substituting the value of $\log k(\theta)$ from (II.4.3) into (II.4.2) allows us to restate the mass action laws as follows: There are constants c_j ($1 \leq j \leq n$) such that if θ is any reaction vector, and if x is any equilibrium composition, then

$$(II.4.4) \quad \sum_{j=1}^n \theta_j (c_j + \log \hat{x}_j) = 0.$$

This form of the mass action law, which is quite equivalent to the standard forms, is more convenient for our purpose.

Another form is often useful for computational purposes. Consider $(c + \log \hat{x})$ as an n -dimensional vector, whose j^{th} component is $c_j + \log \hat{x}_j$. If we also think of the rows a_i of the matrix A as n -vectors, then (II.4.4) may be restated as: If x is an equilibrium composition, then $(c + \log \hat{x})$ is orthogonal to every vector a which is in turn orthogonal to all the vectors a_i . But it follows

from elementary linear algebra that this condition is satisfied if and only if $(c + \log \hat{x})$ is representable as a linear combination of the rows a_i of A . That is, condition (II.4.4) is satisfied if and only if there exists a vector $\pi = (\pi_1, \pi_2, \dots, \pi_m)$ such that, in matrix notation,

$$(II.4.5) \quad c + \log \hat{x} = A^T \pi.$$

5. The Gibbs Free Energy Function

We will have frequent occasion to refer to the free energy of a system. In Section IV we will discuss this more fully; for now, we note that since we are dealing with ideal systems with each phase at constant temperature and pressure, the free energy may be written as a function of composition as follows [6], [7]:

$$(II.5.1) \quad F(x) = \sum_{j=1}^n x_j (c_j + \log x_j).$$

The numbers c_j are called free energy parameters, but still they satisfy (II.4.3).

The least-action principle ([6], p. 29) for the free energy states that the system is in equilibrium if and only if its free energy is a minimum, subject to the constraints (II.2.1-2); that is, a composition vector x^0 represents an equilibrium state if and only if $F(x^0) \leq F(x)$ holds for all states x which satisfy the conditions (II.2.1) and (II.2.2) and which are sufficiently close to x^0 .

Note that the least-action principle, as stated here, requires only that F have a local minimum at x^0 . However, it has been shown ([2], Theorem 8.13, p. 368) that $F(x)$ is convex on its domain—the nonnegative orthant—so that every local minimum is in fact a global minimum, and the underlined phrase above can be eliminated.

6. Relation of Gibbs Function to the Mass Action Laws

Let x be a composition vector of the system satisfying the mass balance laws (II.2.1) and the nonnegativity conditions (II.2.2). Such a composition vector we shall call feasible. We wish to demonstrate that x either satisfies both the mass-action laws ((II.4.4) or (II.4.6)) and the least-action principle for the free energy, or that x satisfies neither. Actually, this is only true when the vector x is positive; i.e., when $x_j > 0$, $j = 1, 2, \dots, n$. If for some j , $x_j = 0$, then the mass-action laws no longer make sense (except in trivial cases), so that no comparison is possible.

This question is dealt with at length in [2]; we will treat here only the simplest case, the case when $x > 0$.

It can be shown that F is minimized at x^0 subject to the constraints (II.2.1) and (II.2.2) if and only if there exists an m -vector π^0 such that x^0 minimizes the Lagrangian function,

$$(II.6.1) \quad L(x, \pi^0) = F(x) - \pi^0(\Lambda x - b)$$

subject only to the nonnegativity conditions (II.2.2).

But x^0 surely cannot minimize $L(x, \pi^0)$ subject to $x \geq 0$ unless for every n -vector θ satisfying $x^0 + t\theta \geq 0$ for $t > 0$ sufficiently small, the derivative of $L(x, \pi^0)$ at x^0 in the direction θ (written $L'_\theta(x, \pi^0)$) satisfies

$$(II.6.2) \quad L'_\theta(x^0, \pi^0) \geq 0.$$

If $x^0 > 0$, then the set of θ we must consider includes every n -vector. Further, it can be shown ([2], Theorem 8.11, p. 368) that for $x^0 > 0$,

$$(II.6.3) \quad L'_\theta(x^0, \pi^0) = \sum_{j=1}^n \theta_j (c_j + \log x_j^0 - A_j^T \pi^0)$$

where A_j denotes the j^{th} column of the matrix A .

Further, from (II.6.3) we see that

$$(II.6.4) \quad L'_{-\theta}(x^0, \pi^0) = -L'_\theta(x^0, \pi^0)$$

so that if (II.6.2) is to be satisfied both for θ and $-\theta$, we must have (if $x^0 > 0$):

$$(II.6.5) \quad L'_\theta(x^0, \pi^0) = 0 \quad \forall \theta \in E^n.$$

But we see from (II.6.3) that (II.6.5) is satisfied for all n -vectors θ if and only if:

$$(II.6.6) \quad c + \log x^0 = A^T \pi^0.$$

Compare the result (II.6.6) with (II.4.5). We have shown that $x^0 > 0$ satisfies the mass action laws if and only if x^0 minimizes the Gibb's function, in each case subject to the constraints (II.2.1) and (II.2.2).

7. Nonideal Chemical Systems

In nonideal chemical systems, only the mass-action laws change. The mass balance laws remain linear. It is usual, however, to cast the mass-action laws into the ideal form by substituting functions called "activities" for concentrations. The "activity" of a species j is thought of as its "effective concentration", when the system has composition x , and is a function of the composition. Thus:

$$(III.7.1) \quad a_j = a_j(x).$$

As will be shown in Section III.7, the activity is a function homogeneous of degree zero in the composition, so that:

$$(III.7.2) \quad a_j(x) = a_j(tx), \quad t > 0.$$

Often, activity coefficients are used. The activity coefficient of species j is simply the ratio between its activity and its concentration.

$$(III.7.3) \quad \lambda_j(x) = \frac{a_j(x)}{x_j}.$$

It can be seen by (III.7.2) and (III.1.2), that $\lambda_j(x)$ is also homogeneous of degree zero.

Using activities, the nonideal mass-action laws may be stated as follows: For any reaction having reaction vector θ , there is an equilibrium constant $k(\theta)$, such that, for any composition vector x representing an equilibrium

state of the system, we have:

$$(II.7.4) \quad \prod_{j=1}^n (a_j(x))^{\theta_j} = k(\theta).$$

The same development as used in Section II.4 can be used to show that there must exist constants c_j^0 such that if x is an equilibrium composition, then there must exist a vector $\pi: (\pi_1, \dots, \pi_n)$ satisfying:

$$(II.7.4) \quad c^0 + \log a(x) = A^T \pi.$$

Alternately, if:

$$(II.7.5) \quad c_j(x) = c_j^0 + \log \lambda_j(x),$$

we may write (II.7.4) as:

$$(II.7.6) \quad c(x) + \log \hat{x} = A^T \pi.$$

It can be shown by the use of (II.7.2) and Euler's Theorem on homogeneous functions (see, for example, [8] p. 234) that if x is strictly positive—i.e., $x > 0$ —then x can satisfy (II.7.4) or (II.7.6) if and only if the function $F(x)$ achieves a minimum at x subject to the mass balance laws (II.2.1), where:

$$(II.7.7) \quad \begin{aligned} F(x) &= \sum_{j=1}^n x_j (c_j^0 + \log a_j(x)) \\ &= \sum_{j=1}^n x_j (c_j(x) + \log \hat{x}_j). \end{aligned}$$

One might argue that some x satisfying (II.7.4) (and

(II.7.6)) might maximize $F(x)$ rather than minimize it. As will be shown later, however, $F(x)$ must be a convex function, ruling out this possibility.

III. THERMODYNAMICS

The Gibbs function is an example of what is known in thermodynamics as a characteristic function. Characteristic functions are the central element in thermodynamics. From the characteristic function of a thermodynamic system, one may compute every quantity of interest to the thermodynamicist. In this section, therefore, we will explore the concept of a characteristic function, and the consequences of the laws of thermodynamics on such functions.

1. Thermodynamic Properties

Properties of a thermodynamic system form the starting point of any study of the system. They are defined (more or less) as the results of certain measurements done on the system, and certain computations done with these measurements. Thermodynamics is the study of the relationships of such properties, although, strictly speaking, at least one property of interest should depend on whether the system is hot or cold.

It is not our purpose to define these properties or to describe their physical interpretations. We are content to list a few of the more common ones. These include composition, volume, pressure, energy, temperature, entropy, enthalpy, chemical potential.

2. The State of a System

Once we have listed all the properties of interest of a thermodynamic system, we note that the various relations among them, as described by thermodynamics, allow some to be computed from the others. Suppose the experimenter chooses from this set of properties T a subset S satisfying the two conditions below:

- (i) Independence — it should not be possible to compute any one of the properties in S from the others in S .
- (ii) Completeness — it should be possible to derive every property in T from a knowledge of only those in S .

Then S is one possible representation of the state of the system. To describe the state of the system one must evaluate each of the properties in S .

From a mathematical point of view, the properties are simply variables, and the state of the system is described by specifying a sufficient number (completeness) of independent variables.

Which of the subsets S satisfying (i) and (ii) is to be chosen is a matter for the thermodynamicist to decide, on the basis of convenience and good taste. Ordinarily he would choose as independent those variables most easily measurable and controllable, so long as this choice does not violate (i) and (ii).

For example, for a chemical system, most of whose phases are liquid and hence incompressible, one would not choose volume as an independent variable. One would, rather, choose to measure and control the pressure of each phase. Similarly, temperature can be controlled and measured more easily than internal energy; hence one chooses the temperature of each phase as another independent variable. The description is completed by specifying the composition of each phase.

In more complex systems, a state description might require additional properties. For a more complete discussion of these matters, see [1], [6].

3. Characteristic Functions

Suppose we have listed for our system all the properties in which we are interested, and have somehow chosen from among them a subset to use as our description of state. We must now somehow relate the state variables (i.e., the properties used in the description of the state) to all the others. This is the duty of the characteristic function, a function of the state of the system from which it is possible, by various manipulations, to compute all the properties of interest which are not themselves state variables.

In [6], p. 24, one may see an example of this. Guggenheim shows there how to compute from the Gibbs function, its derivatives of various orders, and the state variables (in this case temperature, pressure, and composition of each phase), such quantities as entropy, enthalpy, volume, energy, chemical potentials, and others.

Every characteristic function of a given system is equivalent to every other; given any characteristic function, explicitly a function of one description of state S_1 , we are told by the implicit function theorem that it can also be considered as a function of any other description of state S_2 . However, for particular systems and particular problems, one characteristic function is usually more convenient than any other. In our case, the Gibbs free energy function has been found most appropriate.

Characteristic functions generally have the interpretation of energy, or something closely related such as energy divided by temperature.

4. The Global Least-Action Principle

One of the uses of a characteristic function is to indicate what changes in a thermodynamic system may occur, and what changes may not. This is because if the thermodynamicist chooses wisely, his characteristic function will obey a global least-action principle.

Given a thermodynamic system, one may observe that its state changes over time. It may be in state s_1 at time t_1 , but in state $s_2 \neq s_1$ at time t_2 . A function F of the state of the system is said to obey the global least-action principle if for any two such states s_1 and s_2 ,

$$F(s_2) < F(s_1).$$

Thus if we consider as the system evolves, that its state is a function of time, then F , also considered a function of time, must be monotone decreasing. (This can be stated as well with F a monotone increasing function of time. Then, of course, $-F$ will be monotone decreasing.)

There is one other condition that F must satisfy if it is to obey the global least-action principle. This is the local least-action principle introduced in Section II. Thus a state s^0 may be a stationary state if and only if F achieves a local minimum at s^0 .

In this section we will show that every characteristic function, if chosen wisely for the system being considered,

obeys the global least-action principle. It is only necessary to assume that the system obeys the second law of thermodynamics. We shall do so only for systems with one phase, and only for the four most widely known and used characteristic functions. In fact, it would be sufficient to demonstrate this for a single characteristic function, and then note that all characteristic functions are equivalent.

We will require the following thermodynamic quantities:

P is pressure

T is temperature

μ_j is the chemical potential of species j, a function of the state of the system.

V is volume

q is heat absorbed by the system

w is work done on the system

x_j is the amount of species j.

The characteristic functions we will consider are:

G is the Gibbs function

H is enthalpy

U is energy

A is the Helmholtz function.

Finally, we require:

S is entropy.

The laws of thermodynamics are concerned with changes in the state of a system. These changes are called processes. It is usually most convenient to consider only infinitesimal processes, about which Guggenheim ([6] p. 12) has this to say:

All the independent infinitesimal processes that might conceivably take place may be divided into three types: natural processes, unnatural processes, and reversible processes.

Natural processes are all such as actually do occur; they proceed in a direction towards equilibrium.

An unnatural process is one in a direction away from equilibrium; such a process never occurs.

As a limiting case between natural and unnatural processes, we have reversible processes, which consist of the passage in either direction through a continuous series of equilibrium states. Reversible processes do not actually occur, but in whichever direction we contemplate a reversible process we can by a small change in the conditions produce a natural process differing as little as we choose from the reversible process contemplated.

When an infinitesimal process occurs in a thermodynamic system, we are told ([6], p. 10) that the change dU in the energy of the system is equal to the sum of the heat absorbed by the system and the work done on it. That is,

$$(III.4.1) \quad dU = q + w.$$

If heat is lost, or if work is done by the system, then q or w appears as a negative number.

The work term w may be related to the pressure and volume of the system ([6], p. 16). Thus:

$$(III.4.2) \quad w = -PdV.$$

If the system expands by an amount dV , its pressure being P , it has done work on its surroundings.

The Second Law of thermodynamics is stated in terms of entropy. It says that any naturally occurring process will increase the entropy of an isolated system. An isolated system is one which neither mass nor energy (in the form of heat or work) is permitted to enter or leave the system.

When the system is not isolated the change in entropy is partitioned into an external and an internal contribution. The external contribution is the ratio of the heat absorbed to the temperature at which the heat is absorbed. The internal contribution is, according to the second law, nonnegative. In general, then, the second law says that for any natural infinitesimal process,

$$(III.4.3) \quad dS \geq q/T.$$

Equality holds for reversible processes.

The entropy function may be considered as a characteristic function, in fact the most convenient characteristic function to use for systems whose energy, volume and material content are constant. Note that this describes an isolated system, for which the second law takes its simplest form. In general given any infinitesimal process, the change in entropy may be computed ([6], p. 23) by the formula:

$$(III.4.4) \quad dS = T^{-1}dU + T^{-1}PdV - T^{-1} \sum_j \mu_j dx_j.$$

Substituting Equations (III.4.1) and (III.4.2) into (III.4.4), we see that:

$$(III.4.5) \quad dS = \frac{q}{T} - T^{-1} \sum_j \mu_j dx_j.$$

Temperature in thermodynamics is absolute temperature. It must always be a positive number. Thus the second law simply states that for any natural process,

$$(III.4.6) \quad \sum_j \mu_j dx_j \leq 0.$$

Equality holds for reversible processes.

As previously mentioned, each characteristic function is particularly well suited for one particular description of the state of the system. If the state of the system is described by the pressure, the temperature and the composition, then the Gibb's function is best. Then for any process,

$$(III.4.7) \quad dG = -SdT + VdP + \sum_j \mu_j dx_j.$$

If the state is described by entropy, pressure and composition, then the enthalpy is best:

$$(III.4.8) \quad dH = TdS + VdP + \sum_j \mu_j dx_j.$$

If the state is described by entropy, volume and composition, the energy is best:

$$(III.4.9) \quad dU = TdS - PdV + \sum_j \mu_j dx_j.$$

Finally, if the state is described by temperature, volume and composition, then the Helmholtz function is best.

$$(III.4.10) \quad dA = -SdT - PdV + \sum_j \mu_j dx_j.$$

Just as the second law stated in terms of entropy takes a particularly simple form in the case of an isolated system, so if it is stated in terms of different characteristic

functions will it take a simple form for other, nonisolated systems. Thus for a system whose temperature and pressure are constant, we look to the Gibb's function. We have $dT = dP = 0$, so that from (III.4.7), dG becomes:

$$(III.4.11) \quad dG = \sum_j \mu_j dx_j.$$

If entropy and pressure are constant, we have $dS = dP = 0$, and the change in enthalpy (III.4.8) becomes:

$$(III.4.12) \quad dH = \sum_j \mu_j dx_j.$$

If entropy and volume are constant, then $dS = dV = 0$, and the change in energy (III.4.9) is just:

$$(III.4.13) \quad dU = \sum_j \mu_j dx_j.$$

And if temperature and volume are constant, then $dT = dV = 0$, and the Helmholtz function (III.4.11) changes by:

$$(III.4.14) \quad dA = \sum_j \mu_j dx_j.$$

If we appeal to Equation (III.4.6), we see that the second law may be restated in a simple form for any system. Given any natural process,

- (a) if the temperature and pressure are constant throughout, then the Gibb's function is monotonically decreasing—i.e., obeys the least-action principle;
- (b) if the entropy and pressure are constant throughout, then enthalpy obeys the least-action principle;
- (c) if entropy and volume are constant throughout, then the energy obeys the least-action principle;
- (d) if temperature and volume are constant throughout, then the Holmholz function obeys the least-action principle.

5. The Form of Characteristic Functions

We may consider a thermodynamic system to be completely defined by its characteristic function F (which obeys the least-action principle), and a set of constraints on the state variables. In the case of chemical system, the characteristic function is the Gibb's function, and the constraints are (1) the mass-balance laws and the non-negativity conditions on the composition variables, and (2) the constraints that pressure and temperature be constant.

If this is all we know about our system, we cannot be content with Guggenheim's classification of infinitesimal processes. Maintaining those definitions as far as possible, we say:

Definition III.5.1: An (infinitesimal) process is a vector θ and an initial state s^0 satisfying the constraints of the system such that $s^0 + t\theta$ also satisfies the constraints for every sufficiently small positive real t .

In our case, the state s includes composition x and temperatures T^α and pressures P^α of each phase. Since the T^α , P^α are constrained to be given constants, a process θ must have its changes in these variables equal to zero. Hence only composition need be considered, and a process reduces to a reaction vector such that $x + t\theta \geq 0$ for $t > 0$ sufficiently small. Such a θ is called admissible at the composition x .

Since the characteristic function satisfies the least-action principle, we know that any process that does occur leads to a decrease in the function. Turning this around, we define:

Definition III.5.2: A process (s^0, θ) is called an n-process (a mnemonic for natural, but a different name to avoid confusion) if:

$$(III.5.1) \lim_{t \rightarrow 0^+} \frac{F(s^0 + t\theta) - F(s^0)}{t} < 0.$$

It is called a u-process (for unnatural) if:

$$(III.5.2) \lim_{t \rightarrow 0^+} \frac{F(s^0 + t\theta) - F(s^0)}{t} > 0.$$

It is called an r-process (for reversible) if:

$$(III.5.3) \lim_{t \rightarrow 0^+} \frac{F(s^0 + t\theta) - F(s^0)}{t} = 0.$$

This definition limits us to those systems whose characteristic functions possess all the limits necessary in the definition; but this includes all the systems that we have ever seen.

The correspondence between Guggenheim's processes and ours is as follows:

- (a) A process is unnatural according to Guggenheim if and only if it is a u-process.
- (b) Every natural process is an n-process.
- (c) Every reversible process is an r-process.

The converses of statements (b) and (c) are not true. Not every process is classified by Guggenheim.

Guggenheim ([6], p. 9) states the first law as follows:

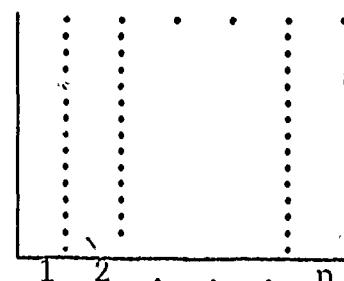
When several systems interact in any way with one another, the whole set of systems being isolated from the rest of the universe, the sum of the energies of the several systems remains constant.

Here the word "isolated" means that neither mass nor energy is permitted to enter or leave the set of systems.

Suppose, however, that we permit energy to enter or leave the set of systems, but close the systems from the entry or exit of mass. Then clearly the first law will still hold for those processes such that no energy actually does enter or leave. We have carefully defined r-processes to satisfy exactly this condition.

The second law, of course, is simply the statement that the characteristic function satisfies the least-action principle for the system under consideration. These two laws have important consequences for the form of the characteristic function.

Consider a chemical system consisting of a single phase, with composition x and characteristic function $G(x)$. We also call $G(x)$ the free energy.



If we divide the phase into n identical parts, then the free energy of each part is the same.

If we again put these parts together, we find the result is indistinguishable from the original phase. What we have done and undone must have been an r-process, so the first law applies. That is, the free energy of the system is conserved, and:

$$G\left(\frac{1}{n}x\right) = \frac{1}{n}G(x).$$

Clearly, $G\left(\frac{1}{n}x\right)$ is the free energy of one of the parts, each of which has composition $\frac{1}{n}x$.

We may take any m of these parts (if we wish, we may let $m > n$) and mix them, and by the same arguments as above,

$$G\left(\frac{m}{n}x\right) = \frac{m}{n}G(x).$$

Characteristic functions are always considered to be continuous. Thus we write that for any nonnegative real number α ,

$$(III.5.4) \quad G(\alpha x) = \alpha G(x).$$

The first law also tells us something about multiphase systems. Let a chemical system have p phases. Let the k^{th} phase have composition vector $x^{(k)}$ and characteristic (or free energy) function $G^{(k)}(x^{(k)})$ when considered as a separate system.

On the other hand, we may consider all the phases together, as though they are a single system. In this case the characteristic function will be $G(x^{(1)}, x^{(2)}, \dots, x^{(p)})$.

But such a conceptual change, being no change at all, is an r-process, and hence conserves free energy. Thus:

$$(III.5.5) \quad G(x^{(1)}, \dots, x^{(p)}) = \sum_{k=1}^p G^{(k)}(x^{(k)}) .$$

Property 1: The free-energy function (or characteristic function) of any chemical system, ideal or not, can be partitioned into a sum of functions, one for each phase of the system. Each of these subfunctions is a function only of the state of the phase for which it is written, and is homogeneous of degree one in the composition of that phase.

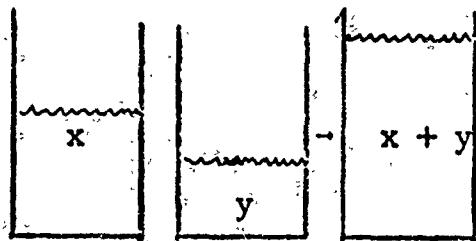
Lemma III.5.3: The ideal Gibbs free energy function, $F(x) = x \cdot (c + \log x)$, has property 1.

Proof: In this case, if $F(x) = \sum_{k=1}^p F^{(k)}(x^{(k)})$, we see that:

$$F^{(k)}(x^{(k)}) = \sum_{j \in [k]} x_j (c_i + \log x_j) .$$

Multiplying each x_j in a compartment by the same factor α changes x_j not at all, so that $F^{(k)}(x^{(k)})$ is clearly homogeneous of degree one. Q.E.D.

Next consider two chemical systems, each with a single compartment. They will have compositions x and y respectively.



We can arrange their free energy functions in a sufficiently general way to insure that the first has free energy $G(x)$, the

second $G(y)$. We can do this by allowing in G for an energy contribution from every species that occurs in either compartment, although any species may be at zero level in one or the other of the compartments.

Experimental evidence indicates that if x is not a scalar multiple of y , then mixing the two compartments together is an n -process. In this event, assuming that $x, y \neq 0$,

$$(III.5.6) \quad G(x + y) < G(x) + G(y) \quad (\text{if } x \neq \alpha y).$$

Definition III.5.4: Let x and y be two composition vectors of a multicompartmented system. Let $x^{(k)}$ be the composition of the k^{th} compartment when the whole system has composition x , and similarly for y . Then x and y are said to be quasi-dependent (written $x \sim y$) if for each compartment $\langle k \rangle$ there exist numbers $\alpha_{\langle k \rangle}, \beta_{\langle k \rangle}$, not both zero, such that:

$$\alpha_{\langle k \rangle} x^{(k)} + \beta_{\langle k \rangle} y^{(k)} = 0 \quad \text{for every compartment } \langle k \rangle.$$

This notation was first introduced in [2], p. 362.

Lemma III.5.5: If $x \sim y$, then for every species j , one of the following holds:

(i) $x_j = y_j$ (if $\bar{x}_{<j>} > 0$ and $\bar{y}_{<j>} > 0$)

(ii) Either $\bar{x}_{<j>} = 0$ or $\bar{y}_{<j>} = 0$ or both.

Proof: Clear from Definition IV.3.2. Q.E.D.

Using the notion of quasi-dependence, and inequality (III.5.6), coupled with the Property 1 in a simple way, we can state:

Property 2: Let x and y be two compositions of a multi-compartmented chemical system with free-energy function G . Then G is linear on the line joining x and y if $x \sim y$, and strictly convex otherwise.

In particular (and much more simply), G is convex.

Lemma III.5.6: $F(x) = x \cdot (c + \log \bar{x})$ has Property 2.

Proof: [2], Theorem 8.13, p. 368.

It should be pointed out here that the author realizes that some substances are only partially miscible. An example is oil and water. One might argue that such a system is an exception to Property 2, since a phase consisting of oil saturated with water cannot be mixed with a phase consisting of water saturated with oil. Indeed, if the attempt is made, the phases will spontaneously separate. Thus the

free energy of the mixture must be greater than the sum of the free energies of the two separate solutions.

This proposed counterexample to Property 2 neglects what was said in Section II.1, that molecules of the same substance but in different phases would be considered as different species. This is not simply a "cheap way out" of the dilemma. A molecule in a solution is not simply an isolated object. It has interactions with other molecules, both like and unlike, in the solution. It is these interactions and the consequent configuration of the potential field surrounding a molecule, as well as the atoms of which it is made, that determine the characteristics necessary to define a species. All these characteristics, save the building blocks of which the molecule is made, are represented by a parameter called the "chemical potential," and which is different for a water molecule surrounded by oil molecules than for a water molecule surrounded by other water molecules.

More detailed information on this point may be obtained from any book on statistical mechanics.

This completes the exposition of the desirable properties of characteristic functions, save for pointing out that it is always assumed that whenever $x > 0$, they are (at least) twice continuously differentiable, and that they are continuous on the entire set $\{x \mid x \geq 0\}$.

The author is grateful to Dr. N. Z. Shapiro for permission to use his results, the derivations of Properties 1 and 2, in this paper.

6. Boundary Behavior of Free-Energy Functions

If we assume that $x > 0$ and compute the partial derivatives of the ideal Gibbs free-energy function, we find that:

$$(III.6.1) \quad \frac{\partial F}{\partial x_j} = c_j + \log \bar{x}_j.$$

If we then allow x_j to approach zero, while retaining $\bar{x}_{<j>} > 0$, we find:

$$(III.6.2) \quad \lim_{\substack{x_j \rightarrow 0 \\ \bar{x}_{<j>} > 0}} \frac{\partial F}{\partial x_j} = -\infty.$$

It appears from various theoretical considerations (e.g., [1], p. 135) that (III.6.2) is generally true for arbitrary free-energy functions.

We have explored this question elsewhere from the point of view of statistical mechanics, and it appears as though the only assumption concerning the behavior of particles in the system one requires in order to prove (III.6.2) is that interactions between pairs of particles are of short range only (and so can be neglected at low concentrations).

Let x be a composition vector, and θ a vector such that $x + t\theta \geq 0$ for sufficiently small positive t . One defines for such pairs x, θ , and for each free-energy function F , the derivative of F at x in the direction θ to be:

$$(III.6.3) \quad F'_\theta(x) = \lim_{t \rightarrow 0^+} \frac{F(x + t\theta) - F(x)}{t}.$$

If we admit extended real numbers then this limit always exists for any free-energy function corresponding to a real physical system. (It must exist for almost all pairs (x, θ) by virtue of the fact that F is convex.)

If we define:

$$I = \{j \mid \bar{x}_{<j>} = 0\}$$

$$J = \{j \mid x_j > 0\}$$

$$K = \{j \mid \bar{x}_{<j>} > 0 \text{ but } x_j = 0\}.$$

then since free-energy functions are always highly differentiable and because of the homogeneity property.

$$(III.6.4) \quad F'_\theta(x) = \sum_{<j> \in I} F^{<j>}(\theta^{<j>}) + \sum_{j \in J} \theta_j \frac{\partial F^{<j>}(x^{<j>})}{\partial x_j}$$

if $\theta_j = 0$ for every $j \in K$, and:

$$(III.6.5) \quad F'_\theta(x) = -\infty$$

if for some $j \in K$, $\theta_j > 0$.

It can be shown ([2], p. 366), that the ideal free-energy function

$$F(x) = \sum_j (c_j + \log x_j)$$

satisfies (III.6.4-5).

It must be pointed out that (III.6.4-5) are only assertions. They cannot be obtained as consequences of previous results.

7. Implications for Chemical Systems

Consider a chemical system with characteristic function $F(x)$. According to Sections II.5 and II.6, this function must be phase separable, and the function written for each phase must be homogeneous of degree one, and strictly convex except on rays passing through the origin.

Let $F^{(k)}(x^{(k)})$ be the function associated with the k^{th} phase. By Euler's Theorem for homogeneous functions, (see [8], p. 234), we may write, for $x^{(k)} > 0$ (the interior of the domain of $F^{(k)}$),

$$(III.7.1) \quad F^{(k)}(x^{(k)}) = \sum_{j \in (k)} x_j \frac{\partial F^{(k)}(x^{(k)})}{\partial x_j}.$$

Summing (III.7.1) over all phases we find:

$$(III.7.2) \quad F(x) = \sum_j x_j \frac{\partial F^{(j)}(x^{(j)})}{\partial x_j}.$$

But by the same argument as produced (III.7.1) we know that:

$$(III.7.3) \quad F(x) = \sum_j x_j \frac{\partial F(x)}{\partial x_j}.$$

Clearly, then, $\frac{\partial F}{\partial x_j} = \frac{\partial F^{(j)}(x^{(j)})}{\partial x_j}$. In addition, since F is homogeneous of degree one, $\frac{\partial F}{\partial x_j}$ must be homogeneous of degree zero.

For each j , we arbitrarily choose a constant c_j , and define:

$$(III.7.4) \quad a_j(x) = \exp \left(\frac{\partial F(x)}{\partial x_j} - c_j \right).$$

Substituting (III.7.4) into (III.7.3) shows that $F(x)$ may be written:

$$(III.7.5) \quad F(x) = \sum x_j (c_j + \log a_j(x)).$$

Compare (III.7.5) and (II.7.7). It is in the manner above that the activities of species in a nonideal chemical system may be computed.

We can see, though, that if the activities are computed in this way, they must satisfy certain conditions.

- (i) From Equation (III.7.4) and the fact that F is phase separable, we find that $a_j(x)$ is homogeneous of degree zero, and depends only on the variables x_k such that $k \in \langle j \rangle$.
- (ii) Since $F(x)$ is convex, we must have

$$(III.7.6) \quad \frac{\partial^2 F(x)}{\partial x_j^2} \geq 0.$$

If the phase $\langle j \rangle$ contains more than one species, then the infinitesimal change implies by partial differentiation is in a direction along which F is strictly convex. Thus the inequality (III.7.6) holds strictly, and:

$$(III.7.7) \quad \frac{\partial^2 F}{\partial x_j^2} = \frac{1}{a_j(x)} \frac{\partial a_j(x)}{\partial x_j} > 0.$$

Since $a_j(x) > 0$ (it is an exponential), $a_j(x)$ must be a strictly increasing function of x_j , other variables being held constant.

(iii) If phase $\langle j \rangle$ contains more than one species, then x_j may tend towards zero while $\bar{x}_{\langle j \rangle}$ remains bounded away from zero. Thus from (III.6.2) we have: (assuming $\bar{x}_{\langle j \rangle} > 0$)

$$(III.7.8) \quad \lim_{x_j \rightarrow 0} \frac{\partial F(x)}{\partial x_j} = \lim_{x_j \rightarrow 0} (c_j + \log a_j(x)) = -\infty.$$

Clearly, then,

$$(III.7.9) \quad \lim_{x_j \rightarrow 0} a_j(x) = 0.$$

Thus the activity, or effective concentration, of a species must be zero when none of that species is present—not a particularly surprising result.

IV. KINETICS

Every chemical system, and likewise every thermodynamic system, is a kinetic system, whose evolution can be described by differential equations called kinetic laws. It is reasonable to ask what kinetic systems correspond to thermodynamic or chemical systems. The method we will use to examine this question will be to construct from the kinetic system a function satisfying the least-action principle. Then if the function also happens to have the appropriate properties, we will know the kinetic system may be considered a thermodynamic one also.

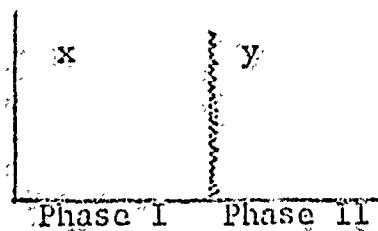
1. Kinetics and the Least Action Principle

The chemical system considered in this section is a special case of what are called primitive systems in [9]. It is a two-phase chemical system satisfying the assumptions:

1. There are no charged species.
2. There is only one possible reaction; the migration of molecules of one particular species from one phase to the other. Molecules of all other species are restricted to remain in the phase they initially occupy.
3. The species in each phase are miscible in all proportions.

We name the two phases Phase I and Phase II. The composition vectors of the two phases will be $x = (x_1, x_2, \dots, x_n)$ and $y = (y_1, y_2, \dots, y_n)$ of Phase I and of Phase II respectively. We consider that a molecule of species j in Phase I (with corresponding composition variable x_j) is chemically indistinguishable from a molecule of species j in Phase II (with composition variable y_j). The only difference is that they occupy different phases. Note that if we wish some nonpermeable substance (i.e., a substance not allowed to pass from one phase to the other) to appear in (say) Phase I only, we

may set the amount of the same substance in Phase II to zero. Thus we are not kept from considering mixtures of very different compositions indeed.



For notational convenience, we assume that it is species 1 in each phase that can migrate to the other phase.

Consider this primitive system as a kinetic system, that is, with its evolution described by differential equations. Further, suppose that the functions expressing the unidirectional flows of species 1 from Phase I to Phase II, and from Phase II to Phase I are known to be J_I and J_{II} respectively, and that:

$$(IV.1.1a) \quad J_I = J(x)$$

$$(IV.1.1b) \quad J_{II} = J(y).$$

Thus, the unidirectional rate of flow of species 1 from one phase to the other is assumed to depend only on the state of that phase from which the flow originates; and the function describing the unidirectional flow is the same regardless of the direction of flow.

Next, we sensibly assume that:

$$(IV.1.2) \quad J(x) > 0$$

for all compositions $x > 0$ (it may be zero if $x_1 = 0$).

Finally, we assume that J is continuously differentiable in each variable, whenever that variable is positive, and to avoid a trivial problem, that the gradient of J is never zero.

Our aim in this section and the next is to construct from this primitive kinetic system a function for which the global least-action principle holds.

We may write the differential equations describing the evolution of this simple system as follows:

$$(IV.1.4) \quad \frac{dx_1}{dt} = J(y) - J(x)$$

$$(IV.1.5) \quad \frac{dy_1}{dt} = J(x) - J(y) = - \frac{dx_1}{dt}.$$

We wish to find a function \tilde{G} corresponding to the function J , such that \tilde{G} has the following properties:

1. \tilde{G} should be phase separable. That is, we assume that \tilde{G} may be written as:

$$(IV.1.6) \quad \tilde{G}(x, y) = G(x) + G(y).$$

We expect the symmetry of \tilde{G} as a consequence of the symmetry of the kinetic system.

2. We assume G to be continuous for $x \geq 0$ and twice continuously differentiable for $x > 0$. Thus we assume that if:

$$(IV.1.7) \quad \dot{\varphi}(x) = \frac{\partial G(x)}{\partial x_1}$$

then $\dot{\varphi}$ and $\nabla \dot{\varphi}$, its gradient, are defined for $x > 0$.

3. We assume \tilde{G} satisfies the global least-action principle with respect to J . Thus:

$$(IV.1.8) \quad \frac{d\tilde{G}}{dt} = \frac{\partial G(x)}{\partial x_1} \frac{dx_1}{dt} + \frac{\partial G(y)}{\partial y_1} \frac{dy_1}{dt} \leq 0.$$

We further assume that \tilde{G} satisfies the global least-action principle with respect to J nontrivially. Thus $\frac{d\tilde{G}}{dt} = 0$ if and only if:

$$\frac{dx_1}{dt} = \frac{dy_1}{dt} = 0.$$

We obtain an immediate consequence of these three assumptions by substituting (IV.1.4-5) and (IV.1.7) into (IV.1.8). After some simple manipulations this yields:

$$(IV.1.9) \quad -\frac{d\tilde{G}}{dt} = [\dot{\varphi}(x) - \dot{\varphi}(y)][J(x) - J(y)] \geq 0.$$

By assumption, we have equality if and only if:

$$J(x) - J(y) = 0.$$

Suppose the states of the two phases are very nearly the same; then we let:

$$x = y + t\theta.$$

Substitute these expressions into (IV.1.9), divide by t^2 , and take the limit as $t \rightarrow 0$. We find, then, that:

$$(IV.1.10) \quad \theta^T (\nabla \phi)^T (\nabla J) \theta \geq 0.$$

We have taken θ to be a column vector; θ^T is its transpose. The gradient vectors $\nabla \phi$ and ∇J are considered to be row vectors, and in (IV.1.10) they are evaluated at the point y .

Equation (IV.1.10) is true for every vector θ , so long as all the partials used exist. (Certainly so long as $y > 0$.) Thus the matrix $(\nabla \phi)^T (\nabla J)$ must be positive semi-definite.

Alternately, we may view (IV.1.10) as requiring that the product of two linear functions of θ be nonnegative. Clearly, this condition is satisfied if and only if $\nabla \phi$ is proportional to ∇J with a nonnegative constant of proportionality. It is obvious that if $\nabla \phi = k \nabla J$ for some $k \geq 0$, then:

$$(IV.1.11) \quad \theta^T (\nabla \phi)^T (\nabla J) \theta = k \|(\nabla J) \theta\|^2 \geq 0.$$

If on the other hand, $(\nabla \tilde{\varphi}) \neq k(\nabla J)$, then since $(\nabla J) \neq 0$ and $(\nabla \tilde{\varphi}) \neq 0$ (else $\nabla \tilde{\varphi} = k(\nabla J)$ with $k = 0$), the two sets $\{\theta | (\nabla J)_\theta = -1\}$ and $\{\theta | (\nabla \tilde{\varphi})_\theta = +1\}$ describe hyperplanes, which by assumption cannot be parallel. At any value of θ where they meet, (IV.5.10) is violated.

Finally, if $\nabla \tilde{\varphi} = k(\nabla J)$ for $k < 0$, then (IV.1.11) is still true with the final inequality reversed. By the assumption that $(\nabla J) \neq 0$, there will exist θ such that $(\nabla J)_\theta \neq 0$. Hence we may easily violate (IV.1.10).

We may therefore write:

$$(IV.1.12) \quad \nabla \tilde{\varphi}(y) = k(y) + \nabla J(y)$$

where $k(y)$ is a nonnegative (scalar) function. (See, for example, [8] p. 322.) To satisfy our condition that G be twice continuously differentiable, we will insist that $k(y)$ be continuous; and to avoid trivial G and satisfy the condition that $\frac{d\tilde{G}}{dt} < 0$ unless $\frac{dx_1}{dt} = \frac{dy_1}{dt} = 0$, we insist that $k(y)$ be strictly positive.

It is convenient, as we shall see, to choose as our integrating function $k(y)$, the function $k(y) = \frac{1}{J(y)}$. Substituting this choice into (IV.1.12) and integrating, we find that:

$$(IV.1.13) \quad \frac{\partial G(y)}{\partial y_1} = \phi(y) = c + \log J(y)$$

where c is a constant of integration.

We cannot for general J explicitly integrate (IV.1.13) to find an equation for G .

2. Generalized Mass-Action Laws

Let us consider a kinetic system with a single reaction,

$$(IV.2.1) \quad \sum_{j=1} r_j N_j \neq \sum_{j=1} p_j N_j.$$

The forward rate of this reaction shall be $J^+(x)$, and the backward rate $J^-(x)$. Thus if species j is a reactant and not a product ($r_j > 0, p_j = 0$), then its rate of disappearance is:

$$(IV.2.2) \quad \left(\frac{dx_j}{dt} \right)_{\text{Dis}} = r_j J^+(x).$$

Similarly, its rate of appearance is:

$$(IV.2.3) \quad \left(\frac{dx_j}{dt} \right)_{\text{Ap}} = r_j J^-(x).$$

If a species j is a product but not a reactant ($r_j = 0, p_j > 0$), then the similar quantities are:

$$(IV.2.4) \quad \left(\frac{dx_j}{dt} \right)_{\text{Dis}} = p_j J^-(x); \quad \left(\frac{dx_j}{dt} \right)_{\text{Ap}} = p_j J^+(x).$$

For species which are both products and reactants ($r_j > 0, p_j > 0$), the appropriate expressions are sums of the above.

As in the previous section, let $G(x)$ be a least-action function for this kinetic system. Then $G(x)$ must satisfy,

$$(IV.2.5) \quad \frac{dG}{dt} = \sum_{j=1}^n \frac{\partial G}{\partial x_j} \frac{dx_j}{dt} \leq 0$$

with equality if and only if $\frac{dx}{dt} = 0$. We may substitute from Equations (IV.2.2-4) into (IV.2.5) to find:

$$(IV.2.6) \quad \sum_{j=1}^n \frac{\partial G}{\partial x_j} [(r_j J^-(x) + p_j J^+(x)) - (r_j J^+(x) + p_j J^-(x))] \leq 0.$$

Collecting terms, we find that:

$$(IV.2.7) \quad \left[\sum_{j=1}^n (r_j - p_j) \frac{\partial G}{\partial x_j} \right] (J^-(x) - J^+(x)) \leq 0.$$

Equality will hold if and only if $J^-(x) = J^+(x)$.

Looking back, one may see that Equation (IV.2.7) is quite similar to Equation (IV.1.9). We define a reaction vector θ as before by:

$$(IV.2.8) \quad \theta_j = (r_j - p_j), \quad 1 \leq j \leq n.$$

Then the development of the last section shows that if we find G satisfying:

$$(IV.2.9) \quad \left(\sum_{j=1}^n \theta_j \frac{\partial G}{\partial x_j} \right) = \log \frac{J^+(x)}{J^-(x)}$$

then G will be a least-action function for the kinetic system.

In fact, this equation is exactly the equivalent of one of the forms of the mass-action laws developed in Section II.4. We have seen (Section II, and [2], p. 360) that the mass-action laws can be stated as follows:

$$(IV.2.10) \quad \prod_{j=1}^n \hat{x}_j^{\theta_j} = k(\theta)$$

where as before θ is a reaction vector. The mass-action laws are such that when they, the mass-balance laws, and the nonnegativity conditions on x are all simultaneously satisfied, then the system is in equilibrium.

These laws are easily derived from ideal chemical kinetics (and from many other forms of chemical kinetics) as follows.

For the reaction (IV.2.1), the simplest form of chemical kinetics (10, p. 10) assumes that the unidirectional rate of disappearance of reactant j can be written:

$$(IV.2.11) \quad \left[\frac{dx_j}{dt} \right]^- = r_j p_1 \prod_{k=1}^n \hat{x}_k^{r_k}$$

and that its unidirectional rate of appearance can be written as:

$$(IV.2.12) \quad \left[\frac{dx_j}{dt} \right]^+ = r_j p_{-1} \prod_{k=1}^n \hat{x}_k^{p_k}$$

(assuming that $p_j = 0$).

The numbers ρ_1 , ρ_{-1} are called respectively the forward and backward rate constants for the reaction. Similar expressions hold for those x_j which are products.

Taking the ratio of (IV.2.11) to (IV.2.12) and noting that at equilibrium species j should appear exactly as fast as it disappears, we see that at equilibrium,

$$(IV.2.13) \quad \prod_{j=1}^n \hat{x}_j^{(r_j - p_j)} = \frac{\rho_{-1}}{\rho_1}.$$

If we let $\theta_j = r_j - p_j$ for each $j = 1, 2, \dots, n$ (as in Section II) and $k(\theta) = \frac{\rho_{-1}}{\rho_1}$, we see that (IV.2.13) is identical to (IV.2.10).

Note that we arrive at the same expression even if we multiply both ρ_{-1} and ρ_1 by an arbitrary positive function.

On the other hand, if the system is not at equilibrium, it is still true that:

$$(IV.2.14) \quad \sum_{j=1}^n \theta_j \frac{\partial F}{\partial x_j} = \log \left[\left(\prod_{j=1}^n \hat{x}_j^{\theta_j} \right) \frac{\rho_1}{\rho_{-1}} \right]$$

where F is the original Gibbs function. It is clear that Equation (IV.2.14) is the same as Equation (IV.2.9) in the case of ideal chemical kinetics, and that the analog of the mass-action law in the case of a more general kinetic system is that if x is any equilibrium composition, then:

$$(IV.2.15) \quad \frac{J^+(x)}{J^-(x)} = 1.$$

3. Kinetic Systems with Several Reactions

In general, a kinetic system will have more than one reaction. Let us say that it has a total of K reactions, numbered $1 \leq k \leq K$, each one of the form:

$$(IV.3.1) \quad \sum_{j=1}^n r_j^{(k)} N_j \neq \sum_{j=1}^n p_j^{(k)} N_j.$$

Typically, an experimenter will not measure the forward and backward rates of each reaction. Instead, using tracers, or some other marking method, he will measure the unidirectional rates of appearance or disappearance of various species. From these quantities we must compute the actual reaction rates.

Clearly, the equations relating the rates of appearance and disappearance of the species and the reaction rates are sums of terms of the sort (IV.2.2-4). Thus:

$$(IV.3.2) \quad \begin{cases} \left(\frac{dx_j}{dt} \right)_{Ap} = \sum_{k=1}^K r_j^{(k)} J_k^-(x) + \sum_{k=1}^K p_j^{(k)} J_k^+(x) \\ \left(\frac{dx_j}{dt} \right)_{Dis} = \sum_{k=1}^K r_j^{(k)} J_k^+(x) + \sum_{k=1}^K p_j^{(k)} J_k^-(x). \end{cases}$$

We assume that the reaction vectors $\theta^{(k)}$ (defined by $\theta_j^{(k)} = r_j^{(k)} - p_j^{(k)}$, $1 \leq j \leq n$) are linearly independent. In this case, whenever Equations (IV.3.2) possess a solution, it will be unique. Thus if we let:

$$(IV.3.3) \frac{dx_j}{dt} = \left(\frac{dx_j}{dt} \right)_{Ap} - \left(\frac{dx_j}{dt} \right)_{Dis} \quad 1 \leq j \leq n$$

then we may write the difference of the two Equations

(IV.3.2) as:

$$(IV.3.4) \frac{dx_j}{dt} = \sum_{k=1}^K \theta_j^{(k)} f_k(x) \quad 1 \leq j \leq n$$

where $f_k(x) = J_k^+(x) - J_k^-(x)$. If (IV.3.4) has a solution (i.e., if $\frac{dx}{dt}$ is a linear combination of the reaction vectors $\theta^{(k)}$), then the solution is unique. A properly formulated kinetic problem will surely possess a solution.

It is a simple matter to substitute the solution $f(x)$ to (IV.3.4) into either of Equations (IV.3.2). We choose to use the second of those equations. Then:

$$(IV.3.5) \left(\frac{dx_j}{dt} \right)_{Dis} = \sum_{k=1}^K r_j^{(k)} f_k(x) - \sum_{k=1}^K \theta_j^{(k)} J_k^-(x).$$

Again, if Equations (IV.3.2) arise from an actual kinetic system, (IV.3.5) must possess a solution $J_k^-(x)$, $1 \leq k \leq K$.

Once we have arrived at expressions for the unidirectional reaction rates J^+ and J^- , we may use the results of the last section. Thus if G is to be the least-action function for this kinetic system, we require that G simultaneously satisfy the K independent equations,

$$(IV.3.6) \sum_{j=1}^n \theta_j^{(k)} \frac{\partial G}{\partial x_j} = \log \frac{J_k^+(x)}{J_k^-(x)} \quad 1 \leq k \leq K.$$

4. Kinetics and Thermodynamics

Given a kinetic system such as that described in the last section, we wish to decide if it may be considered a thermodynamic system. To be so considered, the function G satisfying conditions (IV.3.6) must have the usual thermodynamic properties: it must be phase separable and homogeneous of degree one; the function $G^{<k>}$ for a particular phase $<k>$ must be strictly convex except on lines through the origin; and $\frac{\partial G}{\partial x_j}$ must behave in the appropriate way as x_j approaches zero. These conditions on G will imply conditions on the kinetic laws J^+ and J^- .

Positivity: For Equation (IV.3.6) to be defined, the ratio

$$\frac{J_k^+(x)}{J_k^-(x)}$$

must be positive. This will be assured if the kinetic system is a real system, for in that case we will have the following: Let the reaction associated with reaction k be:

$$\sum_{j=1}^n r_j^{(k)} N_j \rightleftharpoons \sum_{j=1}^n p_j^{(k)} N_j$$

with forward reaction rate $J_k^+(x)$, and backward rate $J_k^-(x)$. Then:

$$(IV.4.1) \quad J_k^+(x) \geq 0 \quad \text{and} \quad J_k^-(x) \geq 0 \quad \forall x,$$

and

$$(IV.4.2a) \quad J_k^+(x) = 0 \quad \text{if and only if} \quad x_j = 0$$

for some j such that $r_j^{(k)} > 0$,

$$(IV.4.2b) \quad J_k^-(x) = 0 \quad \text{if and only if} \quad x_j = 0$$

for some j such that $p_j^{(k)} > 0$.

Continuity and Differentiability: We will insist that G be twice continuously differentiable for $x > 0$, and continuous for $x \geq 0$. One sees immediately from (IV.3.6) that if this is so, then

$$\log \left(\frac{J_k^+(x)}{J_k^-(x)} \right)$$

must be continuously differentiable for $x > 0$. It is not true that

$$\log \left(\frac{J_k^+}{J_k^-} \right)$$

must be continuous for $x \geq 0$.

Homogeneity and Phase Separability: If G is to be homogeneous of degree one and phase separable, then $\frac{\partial G}{\partial x_j}$ must be homogeneous of degree zero and phase separable. From (IV.3.6) we see that for the kinetic system to be considered a thermodynamic system, the kinetic laws J_k^+ and J_k^- must satisfy the following conditions: Let x and y satisfy:

$$(IV.4.3) \quad x_j \bar{y}_{<j>} = y_j \bar{x}_{<j>} \quad 1 \leq j \leq n.$$

One may easily verify that G should be linear on the line joining x and y . Hence along that line, $\frac{\partial G}{\partial x_j}$ must be constant. Thus (IV.3.6) implies:

$$(IV.4.4) \quad \log \left(\frac{J_k^+(x)}{J_k^-(x)} \right) = \log \left(\frac{J_k^+(y)}{J_k^-(y)} \right).$$

Notice that neither $J_k^+(x)$ nor $J_k^-(x)$ need be homogeneous of any degree. The restriction is on their ratio only.

Convexity: Let θ be any reaction vector. Clearly we may express θ as a linear combination of the vectors $\{\theta^{(k)}\}_{k=1}^K$. We suppose that:

$$(IV.4.5) \quad \theta = \sum_{k=1}^K v_k \theta^{(k)}.$$

If G is to be convex, we know that:

$$(IV.4.6) \quad \frac{d^2}{ds^2} G(x + s\theta) \Big|_s = \theta^T (\nabla^2 G(x)) \theta \geq 0$$

where $\nabla^2 G$ is the matrix of second partial derivatives of G . Substituting (IV.4.5) into (IV.4.6) we find that:

$$(IV.4.7) \quad \sum_{k=1}^K v_k \sum_{i=1}^n \theta_i^{(k)} \frac{\partial}{\partial x_i} \left(\sum_{\ell=1}^K v_{\ell} \left[\sum_{j=1}^n \theta_j^{(\ell)} \frac{\partial G}{\partial x_j} \right] \right) \geq 0.$$

The quantity in square brackets is recognizable from (IV.3.6) as

$$\log \left(\frac{J_{\ell}^+(x)}{J_{\ell}^-(x)} \right).$$

Therefore, if we define:

$$(IV.4.8) \quad \mu_{kl}(x) = \sum_{i=1}^n \theta_i^{(k)} \left(\frac{1}{J_{\ell}^-(x)} \frac{\partial J_{\ell}^+(x)}{\partial x_i} - \frac{1}{J_{\ell}^+(x)} \frac{\partial J_{\ell}^-(x)}{\partial x_i} \right)$$

and if the matrix $U(x)$ is taken to be a $K \times K$ matrix whose kl^{th} element is μ_{kl} , then (IV.4.6) simply states that $U(x)$ is a positive semidefinite matrix.

We also know that G is to be strictly convex wherever phase-separability and homogeneity do not imply that it is linear. Thus for any vector v_i (v_1, v_2, \dots, v_k),

$$(IV.4.9) \quad v^T (U(x)) v > 0$$

whenever $\theta = \sum_{k=1}^K v_k \theta^{(k)}$ fails to satisfy:

$$(IV.4.10) \quad \bar{\theta}_{<j>} x_j = \theta_j \bar{x}_{<j>} \quad 1 \leq j \leq n.$$

But what if θ satisfies (IV.4.10)? In that case we notice that:

$$(IV.4.11) \quad \sum_{k=1}^n v_k \mu_{k\ell} = \sum v_k \theta^{(k)} \left[\nabla \log \left(\frac{J_\ell^+(x)}{J_\ell^-(x)} \right) \right] \\ = \frac{d}{ds} \left(\log \frac{J_\ell^+(x + s\theta)}{J_\ell^-(x + s\theta)} \right) \Big|_{s=0} \\ = 0$$

due to condition (IV.4.4). Hence for those v we must have $v^T U(x)v = 0$, as required.

It can easily be verified that in the case of the primitive kinetic system of Section IV.1, Equation (IV.4.6) reduces to the condition that the rate of flow of a species out of its phase must be a monotone increasing function of the amount of that species present, other things being equal.

Notice also that $U(\cdot)$ must be a symmetric matrix. Thus:

$$\begin{aligned}
 \text{(IV.4.12)} \quad \mu_{kl} &= \sum_{i=1}^n \theta_i^{(k)} \left(\frac{1}{J_l^+(x)} \frac{\partial J_l^+}{\partial x_i} - \frac{1}{J_l^-(x)} \frac{\partial J_l^-}{\partial x_i} \right) \\
 &= \sum_{i=1}^n \theta_i^{(k)} \frac{\partial}{\partial x_i} \left(\sum_{j=1}^n \theta_j^{(l)} \frac{\partial G}{\partial x_j} \right) \\
 &= \sum_{j=1}^n \theta_j^{(l)} \frac{\partial}{\partial x_j} \left(\sum_{i=1}^n \theta_i^{(k)} \frac{\partial G}{\partial x_i} \right) \\
 &= \sum_{j=1}^n \theta_j^{(l)} \left(\frac{1}{J_k^+(x)} \frac{\partial J_k^+}{\partial x_j} - \frac{1}{J_k^-(x)} \frac{\partial J_k^-}{\partial x_j} \right) \\
 &= \mu_{lk}.
 \end{aligned}$$

Boundary Behavior: For some fixed k , let $\theta_j^{(k)} > 0$. (We could as easily use some $\theta_j^{(k)} < 0$.) Let x be such that each x_i is greater than zero, $i \neq j$ and x_j tends toward zero. Then we must have:

$$\text{(IV.4.13)} \quad \lim_{\substack{x_j \rightarrow 0 \\ x_i > 0, i \neq j}} \sum_{i=1}^n \theta_i^{(k)} \frac{\partial G}{\partial x_i} = -\infty.$$

Substituting from (IV.3.6) we find that the kinetic system cannot be a thermodynamic system unless:

$$\text{(IV.4.14)} \quad \lim_{\substack{x_j \rightarrow 0 \\ x_i > 0, i \neq j}} \left(\log \frac{J_k^+(x)}{J_k^-(x)} \right) = \begin{cases} -\infty & \text{for } \theta_j^{(k)} > 0 \\ \infty & \text{for } \theta_j^{(k)} < 0. \end{cases}$$

Consider the condition:

$$\sum_{j=1}^n r_j^{(k)} N_j \leq \sum_{j=1}^n p_j^{(k)} N_j.$$

Clearly, for any species j such that $r_j^{(k)} > 0$ and $p_j^{(k)} = 0$, or for which $r_j^{(k)} = 0$ and $p_j^{(k)} > 0$, Equations (IV.4.2a-b) imply (IV.4.14). Only in the case that both $r_j^{(k)} > 0$ and $p_j^{(k)} > 0$, and $r_j^{(k)} \neq p_j^{(k)}$ does (IV.4.14) constrain the kinetic system.

Cycling: Suppose there is an x^0 such that if the kinetic system is initially at x^0 then it will eventually return to x^0 , having passed through states $y \neq x^0$. This phenomenon is called cycling. A kinetic system which can cycle cannot be a thermodynamic system, for the thermodynamic function G would have to decrease strictly throughout the cycle, and the value of G would not be well defined at any point y in the cycle.

Even when the kinetic laws J^+ and J^- satisfy all the above criteria—positivity, differentiability, etc.—it may be difficult to construct a function G for the thermodynamic system. Indeed, we have not established that for all such J a function G must exist.

When a kinetic system does admit a thermodynamic description, however, there is some assurance that its least-action function may be interpreted as a measure of

free, or usable, energy. One can imagine, for example, a machine whose motive power is obtained from a reaction proceeding in one direction faster than the other, and which yields useful work in the process. Thus there is some physical, as well as a mathematical basis for calling a kinetic system that admits this type of description a thermodynamic system.

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13. ABSTRACT <p>A chemical system may be described as different amounts of various chemical species partitioned into a number of homogeneous phases. The species are, in general, not independent. Some species may migrate from one phase to another, and chemical reactions may occur. Thus the system may evolve, the composition of each phase changing as a function of time.</p> <p>One question ordinarily asked of such a system is: "What is the stationary composition?". If the system is mathematically described in the way favored by the classical chemist, the stationary composition will be found by solving a set of equations, some linear (the mass-balance laws) and some nonlinear (the mass-action laws). The investigator may instead describe the system in terms of differential equations - i.e., as a kinetic system. Then he will find the stationary composition by integrating the differential equations from a known initial point to a remote future time. From the point of view of the thermodynamicist, the system displays a perverse desire to minimize its usable (or free) energy. Thus, a function of composition which measures the free energy should achieve a minimum (subject to the mass-balance constraints) at the stationary composition.</p> <p>Each way of viewing the system has implications for the others. The mass-action laws, for example, are mathematically equivalent to the condition that free energy be minimized. The kinetic equations describing the system must satisfy certain conditions implied by the laws of thermodynamics. And the mass-action laws may be derived directly from the kinetic equations.</p> <p>The ideas discussed in this paper can be useful in the mathematical modelling of complex chemical and physiological systems. Physiological systems in particular are most often described using kinetic equations, which have the advantage of describing the mechanisms by which various processes occur, and the disadvantage of being computationally unwieldy. The results in this paper may be used to convert unwieldy kinetic descriptions into more convenient thermodynamic ones, to which the techniques of operations research can be applied.</p>		

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